

Chlor-alkali Industry

The three electrolysis methods used to extract sodium hydroxide is the mercury process, the diaphragm process, and the membrane process.

The Mercury Process

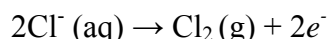
The Mercury process involves the use of a mercury cell undergoing electrolysis to split sodium chloride (common salt) to form sodium hydroxide. This is commonly referred to as the Castner-Kellner process. The mercury cell uses liquid mercury as a cathode as the sodium is reduced and simultaneously incorporated into the mercury, forming an amalgam, or solution. Brine (saltwater) is flowed slowly through the tank with chlorine given off as a gas collected from the top. The top chamber is known as the electrolysis cell and the lower chamber only contains pure water.

At the cathode (located in the top chamber on the diagram with mercury flowing counter clock-wise):



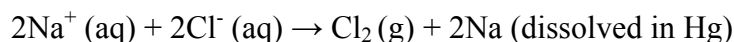
The mercury flows across a sloping floor in the chamber with the negative terminal of the voltage source immersed in it. The amalgam does not react with the brine water due to the applied voltage.

At the anode (also located in the top chamber in the diagram being either a carbon block or can be titanium):

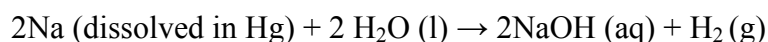


The chlorine gas created from the oxidation is taken off and collected. The anodes are suspended quite close to the mercury to produce large current flows.

The overall reaction in the top chamber is:



The mercury with the sodium dissolved in it then flows into the lower chamber, which only contains water. Without any electrical potential between the water and the amalgam, sodium reacts with water to form sodium hydroxide, as pure sodium reacts:



The amalgam flows in a clockwise direction while the water flows anti-clockwise. The water reacts with the dissolved sodium. This forms sodium hydroxide solution and hydrogen gas. The sodium hydroxide solution flows out on the left while the hydrogen gas is taken away and collected and compressed into cylinders or piped to

another factory. The sodium hydroxide is then drained off and replaced by water. By the time the sodium has reacted the mercury has left the tank so the mercury can be reused back in the electrolysis cell, or upper chamber.

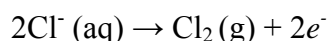
Mercury cells are generally one large cell (as shown in the diagram below) about 15 m long and 1 m wide. It operates between 3 and 4 V which is a small amount compared to the amount of electricity used in factories. The solution is concentrated to about 50% and sold as such or evaporated to dryness to form a solid product. There is no contamination of the product with chloride due to pure water reacting with the mercury amalgam.

The advantages of this process are that it produces very pure sodium and it avoids using asbestos. The disadvantage, however, is that mercury is lost to the environment sometimes as much as 100 to 200g per tonne of NaOH produced. Theoretically, the mercury should just be recycled indefinitely, as it is pumped back into the cell. However, there is an unavoidable mechanical transfer of mercury to the brine solution, which is discharged into the environment back to the ocean. Metallic mercury is extremely insoluble, so it would not pose a problem if it just remained at the bottom of the ocean. Despite this, there are some bacteria that convert mercury into compounds such as dimethyl mercury, which can be taken up by organisms and passed along the food chain with the concentration amplified along the way. The result is consumers who eat fish can receive doses of mercury which affects the nervous system, leading to brain damage. This has resulted in a limitation placed on the amount of mercury discharged with a limit of 1g per tonne of NaOH produced. This is difficult to meet so fewer mercury cells are being built.

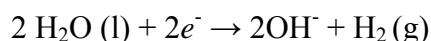
The Diaphragm process

The diaphragm process used inert electrodes – a titanium electrode to withstand attack from the chlorine formed and an iron mesh cathode, which is not affected by the hydroxide solution.

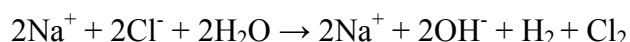
The chloride ions migrate to the anode and are oxidised to chlorine gas. Therefore the reaction at the anode is as follows:



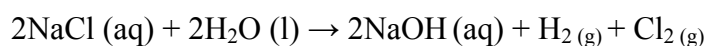
The sodium ions migrate to the cathode but they are too stable to be reduced: instead water is reduced to hydrogen gas and hydroxide ions and so a solution of sodium hydroxide is formed. Therefore at the cathode the reaction that takes place is:



The overall reaction of this, including the spectator ions is as follows:



The complete ionic equation with neutral species is as follows:



The electrolysis produces chlorine and hydrogen gases and leaves behind a solution of sodium hydroxide. The process is producing both chlorine and sodium hydroxide. This is often referred to as **chlor-alkali** industry as both products are equally important. Hydrogen is also sold to other industries that need it (such as hydrogenation of oils for margarine etc). Practical problems that need to be addressed in the design of the cell include: keeping the gasses H_2 and Cl_2 separated as they react vigorously if in contact; minimising contact between hydroxide ion and chlorine in solution as OH^- and Cl_2 forms unwanted chlorite, ClO^- ; and minimising the amount of chloride present in the final hydroxide solution.

The diagram below demonstrates the structure of a diaphragm cell. The diaphragm is a porous barrier between the anode and cathode compartments intended to allow sodium ion flow through to balance the charge of the hydroxide ion formed and complete the flow of electricity in the circuit also allowing a build up of sodium hydroxide in the cathode compartment. The diaphragm is made of asbestos, which is not damaged by the hydroxide solution. The gaseous chlorine in the anode compartment depletes the brine solution of chloride resulting in a slow flow of fresh brine into this compartment and removal of depleted brine. A barrier separates the H_2 and Cl_2 gases so they can be used in other industries.

The voltage across the electrodes is between 3.5 and 5 V. Each cell is quite small so that the gap between the electrodes and the diaphragm is small which will maximise current flow. Large number of cells are assembled together so that products are fed into the same collection areas and there only needs to be one take off point for each product and one input point for brine.

The solution taken at the end has both sodium hydroxide and sodium chloride. Water is evaporated from this solution until the mass is 50% of sodium hydroxide. At this stage, most of the sodium chloride has crystallised so it can be filtered off and the solution of nearly pure sodium hydroxide can be sold or evaporated to dryness (like in the mercury cell) to produce solid sodium hydroxide. The product contains about 1 to 2% sodium chloride.

The advantages of this process is that large quantities of sodium hydroxide can be produced and chlorine, which are two high-demand industrial chemicals, at reasonable costs and at quite acceptable levels of purity. The disadvantages, however, is that: there is always a small amount of chloride in the NaOH produced there are health and environmental problems with small losses of asbestos in making and using diaphragms; there may be hypochlorite, a strong oxidant, in the waste brine solution and this needs to be removed before the brine is discharged into the environment.

The Membrane Process

A membrane cell is a diaphragm cell with an improved diaphragm called a 'membrane'. This is made from polytetrafluoroethylene (PTFE), making it a plastic membrane, which has been modified to include anionic groups to act as an ion exchange membrane. This allows sodium ions to pass through it but not chloride or hydroxide ions. PTFE is very inert and so can stand immersion in hydroxide solutions

for long periods of time. Therefore, the same reactions occur as above in the diaphragm cell but there is no by-product of sodium chloride due to the membrane preventing the chloride and hydroxide ions to pass through.

The use of this process results in virtually pure sodium hydroxide (only contains about 0.02% of sodium chloride at most) being produced as there is no contamination by chloride, and there is virtually no oxidant in the spent brine. Furthermore, there is no working hazard of working with asbestos or mercury.

This process of using electrolysis to develop sodium hydroxide, has been adapted in all **chlor-alkali** plants due to its very pure **production** of sodium hydroxide, similar costs to that of the diaphragm cell (reasonable) and it has no negligible environmental impact. The advantages are much more preferable to that of the mercury and diaphragm process and the membrane process has negligible disadvantages proving to be the best technique for extracting sodium hydroxide

Chlor/alkali manufacturing process

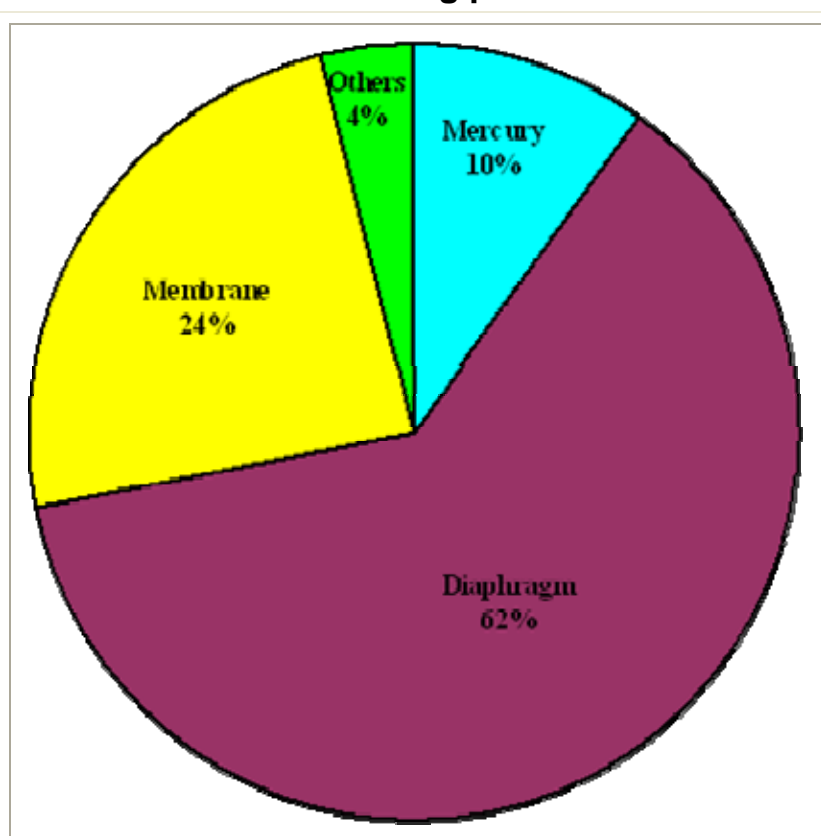


Fig. 4. Chlorine cell technology in the U.S.

The chlor-alkali (also called "chlorine-caustic") industry is one of the largest electrochemical technologies in the world. It is an energy intensive process and is the second largest consumer of electricity (2400 billion kWh) among electrolytic industries. In 2006, about 84% of the total world chlorine capacity of about 59 million metric tons was produced electrolytically using diaphragm and membrane cells, while about 13% was made using mercury cells (Figure 4).

Chlorine is produced by the electrolysis of sodium chloride (common table salt) solution, often called "brine." Thus, when sodium chloride is dissolved in water, it dissociates into sodium cations and chloride anions. The chloride ions are oxidized at the anode to form chlorine gas and water molecules are reduced at the cathode to form hydroxyl anions and hydrogen gas. The sodium ions in the solution and the hydroxyl ions produced at the cathode constitute the components of sodium hydroxide formed

during the electrolysis of sodium chloride. (The chemical reactions occurring in the cell are shown in the Appendix.)

Chlorine is produced electrolytically using three types of electrolytic cells. The main difference in these technologies lies in the manner by which the chlorine gas and the sodium hydroxide are prevented from mixing with each other to ensure generation of pure products. Thus, in diaphragm cells, brine from the anode compartment flows through the separator to the cathode compartment, the separator material being either asbestos or polymer-modified asbestos composite deposited on a foraminous cathode. In membrane cells, on the other hand, an ion-exchange membrane is used as a separator. Anolyte-catholyte separation is achieved in the diaphragm and membrane cells using separators and ion-exchange membranes, respectively, whereas mercury cells contain no diaphragm or membrane and the mercury itself acts as a separator. The anode in all technologies is titanium metal coated with an electrocatalytic layer of mixed oxides. All modern cells (since the 1970's) use these so-called "dimensionally stable anodes" (DSA). Earlier cells used *carbon* based anodes. The cathode is typically steel in diaphragm cells, nickel in membrane cells, and mercury in mercury cells. These cell technologies are schematically depicted in Figures 5-7 and are described below.

Mercury cells

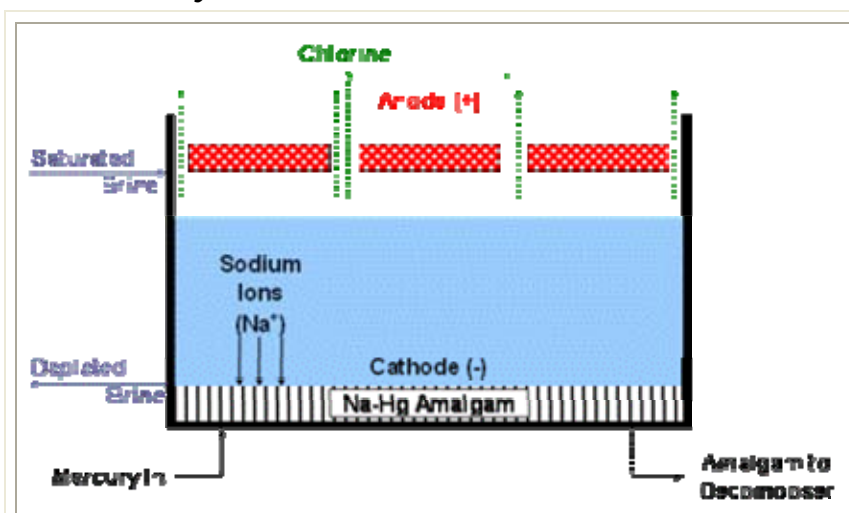


Fig. 5. Schematic of a mercury cell.

The mercury cell has steel bottoms with rubber-coated steel sides, as well as end boxes for brine and mercury feed and exit streams with a flexible rubber or rubber-coated steel cover. Adjustable metal anodes hang from the top, and mercury (which forms the cathode of the cell) flows on the inclined bottom.

The current flows from the steel bottom to the flowing mercury.

Saturated brine fed from the end box is electrolyzed at the anode to produce the chlorine gas, which flows from the top portion of the trough and then exits. The sodium ion generated reacts with the mercury to form sodium amalgam (an alloy of mercury and sodium), which flows out of the end box to a vertical cylindrical tank. About 0.25% to 0.5% sodium amalgam is produced in the cell. The sodium amalgam reacts with water in the decomposer, packed with graphite particles and produces caustic soda and hydrogen. Hydrogen, saturated with water vapor, exits from the top along with the mercury vapors. The caustic soda then flows out of the decomposer as 50% caustic. The unreacted brine flows out of the exit end box. Some cells are

designed with chlorine and anolyte outlets from the end box, which are separated in the depleted brine tank. The mercury from the decomposer is pumped back to the cell.

Diaphragm cells

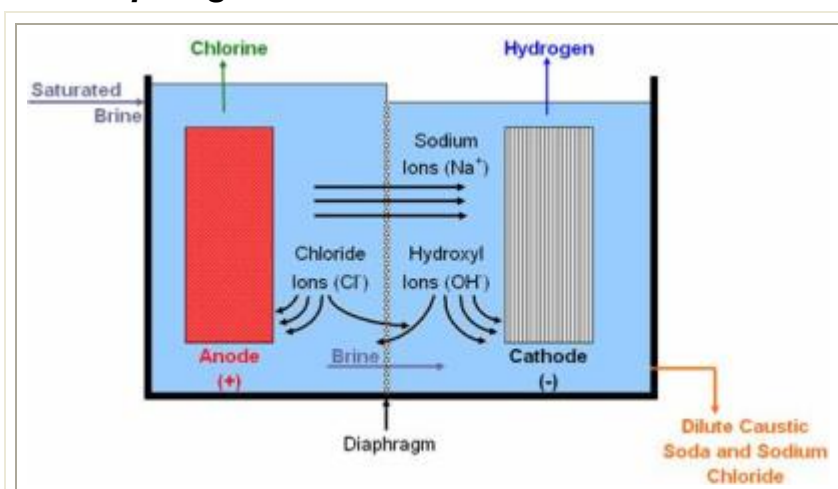


Fig. 6. Schematic of a diaphragm cell.

The diaphragm cell is a rectangular box with metal anodes supported from the bottom with copper-base plates, which carries a positive current. The cathodes are metal screens or punch plates connected from one end to the other end of the rectangular tank. Asbestos, dispersed as a slurry in a bath, is vacuum

deposited onto the cathodes, forming a diaphragm. Saturated brine enters the anode compartment and the chlorine gas liberated at the anode during electrolysis, exits from the anode compartment. It is saturated with water vapor at a partial pressure of water over the anolyte. The sodium ions are transported from the anode compartment to the cathode compartment, by the flow of the solution and by electromigration, where they combine with the hydroxyl ions generated at the cathode during the formation of the hydrogen from the water molecules. The diaphragm resists the back migration of the hydroxyl ions, which would otherwise react with the chlorine in the anode compartment. In the cathode compartment, the concentration of the sodium hydroxide is ~12%, and the salt concentration is ~14%. There is also some sodium chlorate formed in the anode compartment, dependent upon the pH of the anolyte.

Membrane cells

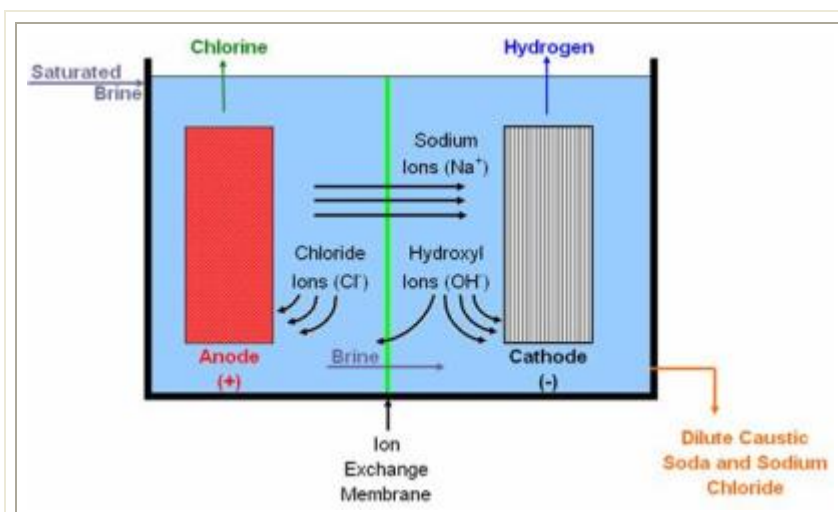


Fig. 7. Schematic of a membrane cell.

In a membrane cell, an ion-exchange membrane separates the anode and cathode compartments. The separator is generally a bi-layer membrane made of perfluorocarboxylic and perfluorosulfonic acid-based films, sandwiched between the anode and the cathode. The

saturated brine is fed to the anode compartment where chlorine is liberated at the anode, and the sodium ion migrates to the cathode compartment. Unlike in the diaphragm cells, only the sodium ions and some water migrate through the membrane. The unreacted sodium chloride and other inert ions remain in the anolyte. About 30-32% caustic soda is fed to the cathode compartment, where sodium ions react with hydroxyl ions produced during the course of the hydrogen gas evolution from the water molecules. This forms caustic, which increases the concentration of caustic solution to ~35%. The hydrogen gas, saturated with water, exits from the catholyte compartment. Only part of the caustic soda product is withdrawn from the cathode compartment. The remaining caustic is diluted to ~32% and returned to the cathode compartment.

Thus, all three basic cell technologies generate chlorine at the anode, and hydrogen along with sodium hydroxide (caustic soda) in the cathode compartment (or in a separate reactor for mercury cells, see Figure 5). The distinguishing difference between the technologies lies in the manner by which the anolyte and the catholyte streams are prevented from mixing with each other. Separation is achieved in a diaphragm cell by a separator, and in a membrane cell by an ion-exchange membrane. In mercury cells, the cathode itself acts as a separator by forming an alloy of sodium and mercury (sodium amalgam) which is subsequently reacted with water to form sodium hydroxide and hydrogen in a separate reactor.

A comparison of the performance characteristics of these three technologies is presented in the Appendix together with schematic process diagram for each of the cell technologies. The primary technology that is presently being used for future expansions or replacements of existing circuits is the membrane cell technology. The major membrane cell technology suppliers, include: Uhde GmbH, Asahi Chemicals, and Chlorine Engineers. DeNora Tech is the sole supplier of diaphragm cell technology. It is highly unlikely that anyone will build a new mercury- or diaphragm-cell plant in the future. Figures 8 and 9 illustrate cell rooms with diaphragm and membrane chlor-alkali cells.

Fig. 8. Chlor-alkali cell room with MDC-55 diaphragm cells (Courtesy of Occidental Chemical Corporation).





Fig. 9. Chlor-alkali cell room with BL-2.7 membrane cells (Courtesy of Uhde GmbH).

Chlorine processing

The chlorine gas from the anode compartment contains moisture, by-product oxygen, and some back-migrated hydrogen. In addition, if the brine is alkaline, it will contain carbon dioxide and some oxygen and nitrogen from the air leakage via the process or pipelines.

Chlorine is first cooled to 60°F (16°C) and passed through demisters to remove the water droplets and the particulates of salt and sodium sulfate. The cooled gas goes to sulfuric acid circulating towers, which are operated in series. Commonly, three towers are used for the removal of moisture. The dried chlorine then goes through demisters before it is compressed and liquefied at low temperatures. The non-condensed gas, called snift gas, is used for producing hypochlorite or hydrochloric acid. If there is no market for hydrochloric acid, the snift gas is neutralized with caustic soda or lime (calcium hydroxide) to form hypochlorite. The hypochlorite is either sold as bleach or decomposed to form salt and oxygen.

Brine processing

Sodium chloride is available in the form of solid salt, mined by excavation or by evaporating seawater. It is also available as a liquid by solution mining the salt domes. The salt has varying concentrations of impurities, which should be removed to operate the electrolytic cells at a high current efficiency. The major impurities are calcium, magnesium, and sulfates. The other minor impurities, which are undesirable, depending upon the type of chlor-alkali process selected, are barium, strontium, manganese, aluminum, silica, iron, vanadium, chromium, molybdenum, titanium, etc.

The solution-mined brine or the solid salt dissolved in the salt dissolver is treated in a reactor with sodium carbonate and caustic soda to precipitate calcium carbonate and magnesium hydroxide (see the Appendix). These precipitates are settled in a settler. The underflow carries the solid slurry, which is pumped to a filter to remove it as

sludge, or sometimes, it is disposed off along with the rest of the liquid effluent from the plant. The calcium carbonate precipitates are heavy, and drag with it the hydroxides of aluminum, magnesium, strontium, etc. The overflow from the settler, which carries ~10-50 ppm (parts per million) of suspended solids, is filtered. For the mercury and the diaphragm cell process, this brine is adequate, and can be fed to the electrolyzers.

In the all cell processes, the filtered brine is heated and passed through a bed of salt in a saturator in order to increase the salt concentration before feeding it to the electrolyzers. In some plants, the brine feed is acidified to improve the cell current efficiency. The acidification reduces the alkalinity, which would otherwise react with the chlorine in the anolyte compartment forming chlorate.

The membrane cell process brine specifications are more stringent than that of the mercury and diaphragm processes, and calls for impurities to be at the parts-per-billion (ppb) level. This is accomplished by filtering the brine in a pre-coat type secondary filter. An ion-exchange resin is used to remove the calcium, magnesium, barium, and iron impurities. It is also possible to remove aluminum by ion exchange. Often, aluminum and silica are removed by adding magnesium chloride in the brine exiting from the salt dissolver.

The depleted brine from the membrane and mercury cell processes carries dissolved chlorine. This brine is acidified to reduce the chlorine solubility, and then dechlorinated in a vacuum brine dechlorinator. The dechlorinated brine is returned to the brine wells for solution mining or to the salt dissolver. If the membrane and diaphragm processes coexist at a given location, the dechlorinated brine can be sent to a saturator for resaturation before being sent to the diaphragm cells.

Sodium hypochlorite manufacturing process

Another useful product generated by the electrolysis of weak brine is sodium hypochlorite, otherwise known as "bleach." Sodium hypochlorite cells generally do not require saturated brine, but can utilize weak brine or even seawater. Bleach is produced "on-site" for disinfection of drinking water and wastewater. The cells employed for this purpose are the same as those used for chlorate manufacture, that is, they consist of an anode and a cathode without a separator or diaphragm. The anodic and the cathodic reactions are the same as in chlor-alkali and chlorate cells, the difference being the pH of the electrolyte, which is maintained in the range of 10 to 12. The electrolytically generated chlorine reacts with sodium hydroxide to form sodium hypochlorite. However, the hypochlorite ion, formed in the bulk, is easily reduced at the cathode to reform chloride. Therefore, only dilute solutions of bleach can be produced in the cell. Hypochlorite can also react further to form chlorate, but this can be minimized by keeping the solution basic and the temperature low (close to room temperature).

There are several manufacturers of seawater electrolysis cells in the market. The best known cells include Seachlor made by DeNora (producing 1000-2500 ppm active chlorine) or Salinec made by Exceltec International Corporation (generating 200-300 ppm active chlorine).

Appendix

Chlor/alkali manufacturing process

Electrochemical and chemical reactions occurring in mercury cells

- [1] $2\text{Cl}^- \Rightarrow \text{Cl}_2 + 2\text{e}^-$ (anodic reaction)
- [2] $2\text{Na}^+ + 2\text{Hg} + 2\text{e}^- \Rightarrow 2\text{Na (in Hg)}$ (cathodic reaction)
- [3] $2\text{Cl}^- + 2\text{Na}^+ + 2\text{Hg} \Rightarrow \text{Cl}_2 + 2\text{Na (in Hg)}$ (overall cell reaction)
- [4] $2\text{Na (in Hg)} + 2\text{H}_2\text{O} \Rightarrow \text{H}_2 + 2\text{NaOH} + \text{Hg}$ (decomposer reaction)
- [5] $2\text{NaCl} + 2\text{H}_2\text{O} \Rightarrow \text{Cl}_2 + 2\text{NaOH} + \text{H}_2$ (overall process reaction)

Electrochemical and chemical reactions occurring in diaphragm and membrane cells

- [1] $2\text{Cl}^- \Rightarrow \text{Cl}_2 + 2\text{e}^-$ (anodic reaction)
- [6] $2\text{H}_2\text{O} + 2\text{e}^- \Rightarrow 2\text{OH}^- + \text{H}_2$ (cathodic reaction)
- [7] $2\text{Cl}^- + 2\text{H}_2\text{O} \Rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{OH}^-$ (overall ionic reaction)
- [5] $2\text{NaCl} + 2\text{H}_2\text{O} \Rightarrow \text{Cl}_2 + 2\text{NaOH} + \text{H}_2$ (overall reaction)
- [8] $\text{Cl}_2 + 2\text{NaOH} \Rightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$ (side reaction)
- [9] $3\text{NaOCl} \Rightarrow \text{NaClO}_3 + 2\text{NaCl}$ (side reaction)

Reaction [9] will contaminate the caustic product with chlorate.

Chemical reactions occurring in brine processing

- [10] $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \Rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$ (CaCO_3 precipitates)
- [11] $\text{MgCl}_2 + 2\text{NaOH} \Rightarrow \text{Mg(OH)}_2 + 2\text{NaCl}$ (Mg(OH)_2 precipitates)

Comparison of cell technologies

	Mercury	Diaphragm	Membrane
Operating current density (kA/m ²)	8 - 13	0.9 - 2.6	3 - 5
Cell voltage (V)	3.9 - 4.2	2.9 - 3.5	3.0 - 3.6
NaOH strength (wt%)	50	12	33-35
Energy consumption (kWh/MT Cl ₂) at a	3360 (10)	2720 (1.7)	2650 (5)

current density of (kA/m ²)			
Steam consumption (kWh/MT Cl ₂) for concentration to 50% NaOH	0	610	180

Process flow sheets

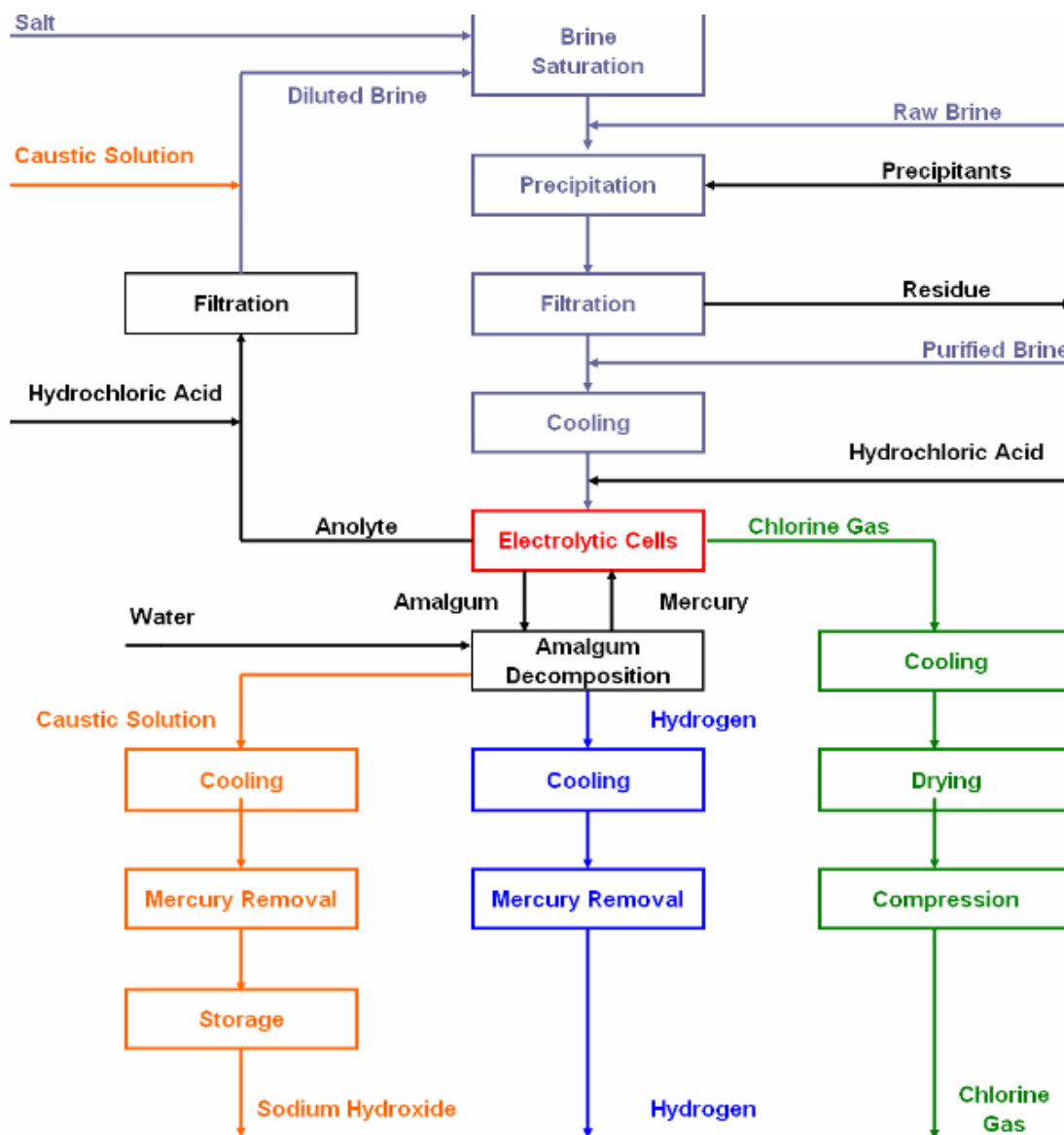


Fig. 12. Mercury cell process flow sheet.

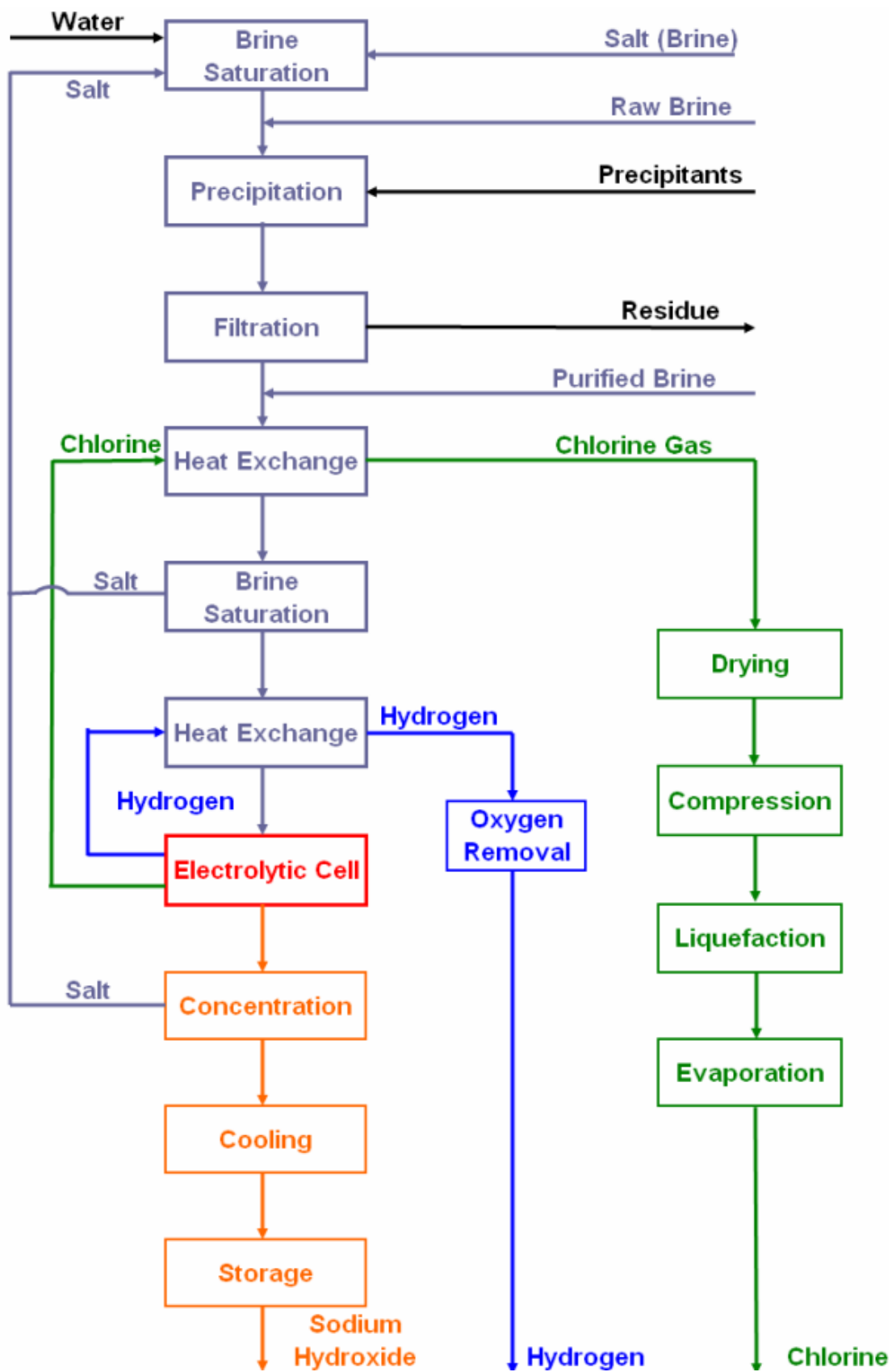


Fig. 13. Diaphragm cell process flow sheet.

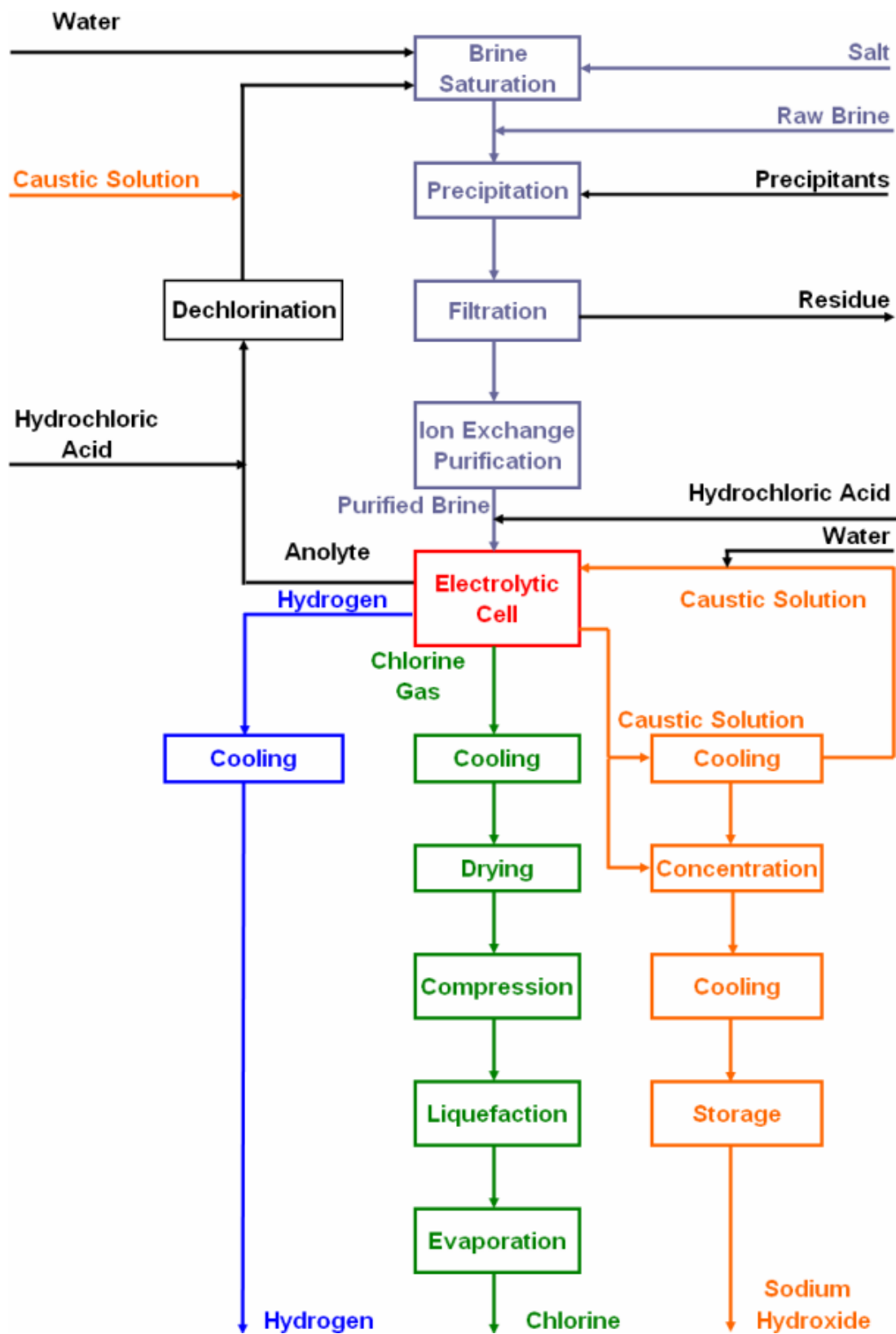


Fig. 14. Membrane cell process flow sheet.

Sodium hypochlorite/chlorate manufacturing process

Electrochemical and chemical reactions occurring in cells

- [1] $2\text{Cl}^- \implies \text{Cl}_2 + 2\text{e}^-$ (anodic reaction)
- [7] $2\text{H}_2\text{O} + 2\text{e}^- \implies 2\text{OH}^- + \text{H}_2$ (cathodic reaction)
- [8] $\text{Cl}_2 + 2\text{OH}^- \implies \text{OCl}^- + \text{Cl}^- + \text{H}_2\text{O}$ (hypochlorite formation)
- [9] $3\text{OCl}^- \implies \text{ClO}_3^- + 2\text{Cl}^-$ (chlorate formation)
- [12] $\text{NaCl} + \text{H}_2\text{O} \implies \text{NaOCl} + \text{H}_2$ (overall hypochlorite reaction)
- [13] $\text{NaCl} + 3\text{H}_2\text{O} \implies \text{NaClO}_3 + 3\text{H}_2$ (overall chlorate reaction)
- [14] $3\text{Cl}_2 + 6\text{NaOH} \implies \text{NaClO}_3 + 5\text{NaCl} + 3\text{H}_2\text{O}$ (chemical chlorate formation)

Hypochlorite formation is promoted by the use of weak brine, basic solution, and low cell temperatures.

Chlorate formation is promoted by the use of saturated brine, acidic solution, and temperatures close to the boiling point of the solution.